Modification of Jojoba Oil for Lubricant Formulations

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Jojoba oil has good lubricity and it can be utilized as a component in lubricating oil formulations. The physicochemical properties of the oil when compared with those of mineral oil base stocks showed that the pour point, acid value and oxidative stability were the limiting factors in its use as a base stock. Studies were carried out to improve these properties. The results indicated that these properties can be modified by physical and chemical methods and also by additive treatment. It has also been possible to increase the viscosity of jojoba oil by partial sulfurization, resulting in widening the scope of its utilization in developing lubricant formulations.

In addition to using petroleum as a major source of energy, its constituents are also utilized for many nonenergy applications, e.g., the production of lubricants, specialty products, additives and petrochemicals. Any shortfall in the production of crude oil (1,2) will equally affect the availability of these products, which are vital for agricultural and industrial production. Further, lubricating oil is produced in India from imported crude oil because indigenous crude is not suitable for the production of high quality lubricating oil, due to poor yield and viscosity (3). Therefore, there is an urgent need to look for alternative sources. One of the approaches to conserve and possibly replace petroleum, in general, is to look for renewable sources of hydrocarbons. One plant with potential for providing a substitute source for lubricating oil base stocks is *Simmondsia chinensis*, commonly known as jojoba. Jojoba oil is unique because it is a wax ester instead of a typical triglyceride. Jojoba wax esters are similar to those in sperm whale oil and can be utilized in areas where sperm whale oil has been used in the past. A lot of research continues on breeding, growing and harvesting to convert jojoba from a wild desert bush to a fully cultivated crop capable of producing a sufficient quantity of seeds every year to serve the market (4). This unique oil has great potential and has been subjected to a variety of transformations.

The potential uses of jojoba oil range from skincare products to food and to high-pressure lubricants. Jojoba oil has been added to conventional crankcase oil with success and can be utilized in other lubrication applications. However, more work needs to be done in this area.

At the Indian Institute of Petroleum, the oil has been studied in detail and compared with mineral oil base stocks for its potential utilization in various lubricant applications. Attempts have been made to improve some of the properties—such as pour point, acid value and oxidative stability—which do not match those of mineral oil base stocks. This paper presents the result of these investigations.

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EXPERIMENTAL

Jojoba seeds were procured from Janca Jojoba Oil and Seed Co., Arizona, USA. After crushing, the seeds were extracted in soxhlet extractors. Two of the commercially available pour point depressants, polyisobutylene (PIB) and polymethacrylate (PMA), compatible with jojoba oil were tried at different concentrations. Besides alkali in refining, clay and bauxite (5) were also used to reduce the free acid content. The two adsorbents were activated at 250°C for 3 hr. Studies on the oxidative stability of jojoba oil were carried out according to the IP 306/82 method. Sulfurized jojoba oils (SJO) were prepared (6,7) by addition of the required amount of sulfur to jojoba oil (A1 to A6) or by the dilution of sulfurized jojoba oils SJO-10 and SJO-26 (prepared by the addition of 10 and 26% sulfur), respectively with jojoba oil.

Jojoba oil was treated with 8% charcoal at 220°C for 2 hr. Caramelization was carried out by heating the oil up to 300°C (in about 26 min), maintaining this temperature for 5 min, then cooling and filtrating.

RESULTS AND DISCUSSION

Of the various solvents studied for the extraction of oil, hexane, heptane and cyclohexane extracted substantially the same amount of oil. However, the yield was somewhat lower with benzene and dichloromethane. Benzene-extracted oil showed some residue on standing for 7-8 days. Such residues were negligible in other solvents. There were no marked differences in the physico-chemical properties of the different oils (Table 1). Hexane was found to be the best solvent for extraction because of its high oil yield, with no tendency to deposit residue on standing. Also, hexane is commonly used in commercial extraction of vegetable oils.

Hexane-extracted oil was compared with mineral oil base stocks (Table 2). The results clearly revealed that the former has high viscosity index, low viscosity, high pour point, and high acid content. The poor oxidation stability, as indicated by high iodine value, limits its utilization as a lubricating oil base stock. If the above properties of the oil could be modified, the scope of its application in lubricant compositions could be widened (8).

Modification of jojoba oil; improvement of properties—pour point. Since the pour point of jojoba oil was high (+9°C), two pour point depressants, PIB and PMA, were tried at different concentrations. There was no change in the pour point. At lower temperatures the microcrystals of wax present in oils swell, forming a sort of web and thus trapping a significant volume of oil. The microcrystals act like a sponge in water. The pour point depressants restrict the growth of microcrystals and thus ensure free flow of oil even at lower temperatures. Jojoba oil being a liquid wax does not support microcrystal growth and there is no interlocking and trapping of oil. In fact, the pour point is actually its freezing point and that is why there was

TABLE 1

Comparison of Physico-Chemical Properties of Jojoba Oil Extracted with Various Solvents

Solvent	Oil %	Residue %	Refractive index 25°C	Specific gravity d_{25}^{25}	Kinematic viscosity cSt 40°C	Kinematic viscosity cSt 100°C	Viscosity index	Saponification value mg KOH/g	Acid value mg KOH/g	Iodine value g/100 g
Hexane	42.5	traces	1.4639	0.8662	24.92	6.43	233	94.69	1.10	82.98
Heptane	41.0	traces	1.4640	0.8650	24.81	6.43	232	84.89	1.14	82.93
Cyclohexane	39.5	traces	1.4648	0.8875	24.07	6.34	236	94.60	1.99	84.40
Benzene	39.4	2.0	1.4636	0.8652	24.66	6.44	235	92.58	1.31	82.34
Dichloro-methane	41.4	traces	1.4638	0.8659	24.66	6.50	238	92.41	1.24	83.04

TABLE 2

Physico-Chemical Characteristics of Jojoba Oil and Mineral Oil Base Stocks

Properties	Jojoba oil	Typical range for mineral oils
Refractive index 25°C	1.4639	—
Specific gravity d25	0.8662	—
Kinematic viscosity cSt		
at 40°C	24.92	—
at 100°C	6.43	5.0-20.0
Absolute viscosity Cp		
at 15.5°C	54.72	—
Surface tension dyne/cm	34.00	—
Viscosity index	233	90-95
Pour point °C	+9	+6 to −40
Carbon residue % wt	0.1	0.1 to 2.0
Copper corrosion	1 a	—
Acid value mg KOH/g	1.10	0.05 to 0.15
Saponification value mg KOH/g	94.69	Nil
Iodine value g/100g	82.98	Nil
Ash max % wt	Nil	0.01 to 0.1

no effect of pour point depressants. However, its pour point can be lowered by blending with mineral oils. The blend of mineral oil (pour point −6°C) and jojoba oil (pour point +9°C) 50:50 had a pour point −3°C. Addition of PIB to the blend at 0.5 and 1.0% concentration levels further reduced the pour point to −6 and −9°C, respectively.

Acid value. The acidity of the oil was on the higher side as compared to that of mineral oil although the copper strip corrosion tests showed that these acids were noncorrosive. Adsorption by contacting or percolation, and washing with alkali were tried to remove the free fatty acids from the oil. For contacting, two samples of clay were studied. Stirring of the oil with 5% activated clay I for 30 min at 100°C resulted in lowering the acid content to 0.3758 mg KOH/g. However, the acid value dropped to 0.2175 mg KOH/g on treating with 15% clay at 150°C. Treatment of the oil with 6% of clay II at 110°C gave better results, bringing down the acid value to 0.1181 mg KOH/g. This value was very near the range specified for mineral oil base stocks.

Percolation of the oil over bauxite was also studied for the removal of free fatty acids. A graph of acid value vs time (Fig. 1) showed a sharp rise in the acidity after 34 hr. The life of the column was found to be 46 hr when liquid hour space velocity was 2.8593 bbl/ton/hr.

Acid content of jojoba oil was brought down to 0.10 mg KOH/g—acidity normally observed in mineral oils used for lubricating oil formulations—by washing the oil four times with 2% sodium carbonate solution, contacting for 1 min each time.

Oxidation stability. Temperature of the oil and metallic components, presence of oxygen, nature of metal and/or debris—all contribute to the oxidative changes of the oil. The major cause for the deterioration of lubricating oils while in service is generally understood to be a process of oxidation. For different applications different methods have been recommended for determining oxidative stability of an oil (9). Resistance to oxidation of oil can be measured by measuring the oxygen absorbed, change in the viscosity and/or acidity. In most of the standard methods used for determining the oxidative stability of mineral oils, large sample size and long test durations are required. The IP 306/82 method was selected for the present stability studies because it requires only small samples and the test duration is only 48 hr. The results are expressed in terms of percentage of volatile acidity, soluble acidity, sludge and total oxidation product of the oil sample with and without a copper catalyst.

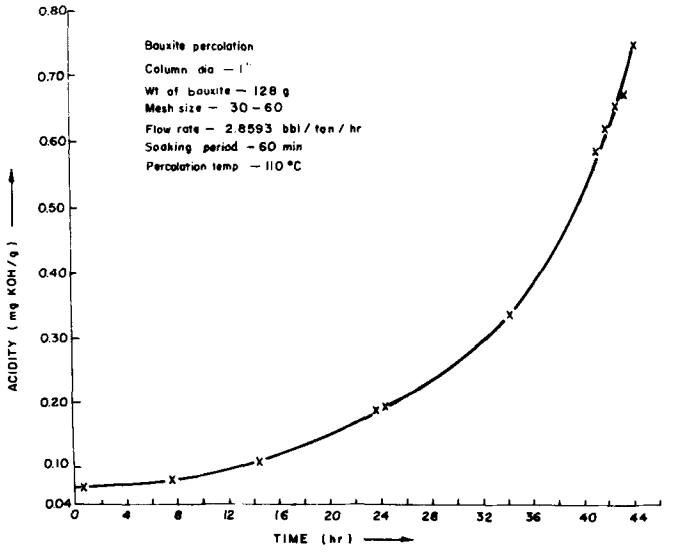

FIG. 1. Removal of free acids from jojoba oil by bauxite percolation; relation between acidity vs time.

Most of the volatile acids may escape the lubrication system during operation but some may condense during shut-down of the equipment. Certain types of oxidation products remain in solution and increase the viscosity and acid value of the lubricant. The nature of acids rather than total value is significant from the point of view of corrosion. Insoluble products form sludge and can clog the filters or oil passages leading to oil starvation in the parts requiring lubrication. The total oxidation products (TOP) give an indication of the overall oxidative stability of the oil. Invariably the values with catalyst are higher and are more relevant as the lubricant is in contact with metals when in use.

Jojoba oil has better oxidative stability than other vegetable oils but is inferior to mineral oil base stocks of both low and high viscosities (Table 3). To improve the stability, effects of refining [with charcoal (10), caramelization (11), clay and bauxite], chemical modification such as sulfurization, blending with mineral oils of high stability and of additive treatment were studied. Refining of raw jojoba oil with clay, bauxite and charcoal (Table 4) resulted subsequently in the increase of total oxidation products in stability tests with or

TABLE 3

Comparative Stability of Jojoba Oil and Mineral Oil Base Stocks

		Volatile acidity mg KOH/g		Soluble acidity mg KOH/g		Total sludge % wt		Total oxidation products %	
		Uncatalyzed	Catalyzed	Uncatalyzed	Catalyzed	Uncatalyzed	Catalyzed	Uncatalyzed	Catalyzed
Mineral oil base stock, low viscosity	i)	0.0067	0.0269	0.1683	0.2692	0.0036	0.0060	0.0597	0.1022
	ii)	0.0112	0.0448	0.2244	0.3366	0.0040	0.0076	0.0795	0.1299
Mineral oil base stock, high viscosity	i)	0.0026	0.0161	0.1122	0.4488	0.0004	0.0076	0.0372	0.1567
	ii)	0.0027	0.0269	0.2019	0.4039	0.0024	0.0112	0.0680	0.1494
Jojoba oil (raw)	i)	0.0056	2.9396	1.0098	13.5760	0.0212	0.0172	0.3469	5.3163
	ii)	0.0065	3.5480	0.9874	12.7459	0.0176	0.0148	0.3365	5.2427

TABLE 4

Effect of Refining Treatments on Stability

	Volatile acidity mg KOH/g		Soluble acidity mg KOH/g		Total sludge % wt		Total oxidation products %	
Sample	Uncatalyzed	Catalyzed	Uncatalyzed	Catalyzed	Uncatalyzed	Catalyzed	Uncatalyzed	Catalyzed
Jojoba oil (raw)	0.0056	2.9396	1.0098	13.5760	0.0212	0.0172	0.3469	5.3163
Refined jojoba oil (clay)	0.0036	5.7895	2.1500	30.0247	0.0048	0.0180	0.6957	11.5091
Refined jojoba oil (bauxite)	3.8776	1.7503	19.2500	35.6700	0.0084	0.0096	7.4290	11.9367
Refined jojoba oil (charcoal)	1.3688	6.1261	11.3254	26.4993	0.0280	0.2160	4.1010	10.6840
Refined jojoba oil (alkali)	9.2228	3.0069	28.2586	10.2259	0.0120	0.0120	12.0381	4.2578
Refined jojoba oil (heat)	8.9311	2.1766	27.2646	12.9030	0.1120	0.0120	11.7256	4.8504

without catalysts. This observation is at variance with the finding of other investigators (10,12) who reported that jojoba oil should be refined before sulfurization to get a stable product. It appears that refining reduced the stability of jojoba oil due to the removal of natural antioxidants (tocopherols and phospholipids) from the oil (13,14). Alkali and heat treatments, on the other hand, improved the oxidative stability (catalyzed) of jojoba oil marginally, but the TOP values obtained with the uncatalyzed samples were very high as compared to raw jojoba oil.

As chemical modification of jojoba oil is bound to reduce the degree of unsaturation, the effect of partial sulfurization was studied (Table 5). There was little change in the stability of jojoba oil. During sulfurization under high temperatures, it is quite possible that the unstable natural antioxidants were destroyed (13,14).

Blending with mineral oil yielded anticipated results (Table 6) and the TOP values could be brought down. However, the degree of improvement depends on the proportion of blending components used. Response of various antioxidants to raw jojoba oil can be assessed from Table 7. Whenever an additive provided a good response, the dosage was optimized. Response studies of three commercial additives (ZDDP, aromatic amine A and a phenolic compound, DBPC widely used for formulating lubricating oils and specialty products) to raw jojoba oil showed that ZDDP gave the lowest values for the catalyzed sample. The amine A oxidation inhibitor did not improve the stability, perhaps because of its poor compatibility. DBPC (phenolic type) was effective but the TOP values obtained were far from those of mineral oil base stocks. p-Toluidine, an effective oxidation inhibitor for vegetable oils, responded more favorably. Of the two diamines with different alkyl chain lengths, amines B and C both responded well with raw jojoba oil and dosage increase marginally improved the stability. Because the stability of refined jojoba oil and chemically modified jojoba oil (sulfurized) was not as good as that of raw jojoba oil to start with, additive treatment was not attempted. Results obtained with blends (raw jojoba oil and mineral oil base stocks 50:50) doped with additives are presented in Table 8. ZDDP, p-toluidine and the diamine inhibitors did not seem to improve the stability of the blend significantly as compared to the values obtained with raw jojoba oil. The antioxidants are selective in their activity in the sense that they improve the stability of either jojoba oil or mineral oil, but not of the blend. The aromatic diamine C appears to be the best additive to improve the stability of jojoba oil and its blend with mineral oil.

Viscosity. For most industrial applications, lubricating oils with viscosities ranging from 5 to 15 cSt

TABLE 5

Effect of Chemical Modification on Stability

	Volatile acidity mg KOH/g		Soluble acidity mg KOH/g		Total sludge % wt		Total oxidation products %	
Sample	Uncatalyzed	Catalyzed	Uncatalyzed	Catalyzed	Uncatalyzed	Catalyzed	Uncatalyzed	Catalyzed
Jojoba oil (raw)	0.0056	2.9396	1.0098	13.5760	0.0212	0.0172	0.3469	5.3163
0.2% sulfurized jojoba oil	0.0269	4.3623	0.8145	14.2920	0.0036	0.0048	0.2735	5.9901

TABLE 6

Stability of Blend

	Volatile acidity mg KOH/g		Soluble acidity mg KOH/g		Total sludge % wt		Total oxidation products %	
Sample	Uncatalyzed	Catalyzed	Uncatalyzed	Catalyzed	Uncatalyzed	Catalyzed	Uncatalyzed	Catalyzed
Jojoba oil (raw)	0.0056	2.9396	1.0098	13.5760	0.0212	0.0172	0.3469	5.3163
Mineral oil base stock (high viscosity 1300N)	0.0026	0.0161	0.1122	0.4488	0.0004	0.0076	0.0372	0.1567
Mineral oil base stock + raw jojoba oil (50:50)	0.0208	2.8590	0.4218	3.4804	0.0200	0.0040	0.1620	2.0380

TABLE 7

Effect of Additive Treatment on Raw Jojoba Oil

Samples	Volatile acidity mg KOH/g		Soluble acidity mg KOH/g		Total sludge % wt		Total oxidation products %	
	Uncatalyzed	Catalyzed	Uncatalyzed	Catalyzed	Uncatalyzed	Catalyzed	Uncatalyzed	Catalyzed
Jojoba oil	0.0056	2.9396	1.0098	13.5760	0.0212	0.0172	0.3469	5.3163
Jojoba oil + ZDDP (0.6%)	0.0026	0.0538	2.8880	2.8139	0.0076	0.0084	0.9350	0.9285
Jojoba oil + aromatic amine-A(0.5%)	7.1718	2.9531	14.5545	15.7147	0.0160	0.3360	6.9870	6.3256
Jojoba oil + hindered phenol(0.5%)	0.0448	1.1893	0.4488	7.7418	0.0200	0.0760	0.1784	2.9416
Jojoba oil + hindered phenol(0.6%)	0.0219	0.4398	0.9896	8.4666	0.0200	0.0320	0.3445	2.8896
Jojoba oil + p-toluidine(0.6%)	0.1099	0.2639	1.3194	0.9896	0.0160	0.1280	0.4746	0.5301
Jojoba oil + aromatic amine-B(0.4%)	0.1099	0.0439	0.4398	0.6597	0.0400	0.1200	0.2164	0.3457
Jojoba oil + aromatic amine-B(0.5%)	0.0897	0.1147	0.8437	0.3164	0.0600	0.1880	0.3395	0.3263
Jojoba oil + aromatic amine-C(0.5%)	0.1463	0.0975	0.6098	0.4878	0.0120	0.0760	0.2546	0.2638
Jojoba oil + aromatic amine-C(0.6%)	0.1979	0.1319	0.5497	0.4398	0.0120	0.0520	0.2519	0.2354

TABLE 8

Effect of Additive Treatment on Blends

Samples	Volatile acidity mg KOH/g		Soluble acidity mg KOH/g		Total sludge % wt		Total oxidation products %	
	Uncatalyzed	Catalyzed	Uncatalyzed	Catalyzed	Uncatalyzed	Catalyzed	Uncatalyzed	Catalyzed
Raw jojoba oil + mineral oil base stock (50:50)	0.0208	2.8590	0.4218	3.4804	0.0200	0.0040	0.1620	2.0380
Raw jojoba oil + mineral oil base stock (50:50) + ZDDP(0.6%)	0.0208	0.0939	1.0546	1.3710	0.0120	0.0400	0.3570	0.5101
Raw jojoba oil + mineral oil base stock (50:50) + p-toluidene (0.6%)	0.0104	0.4382	0.4219	3.3222	0.0040	0.1400	0.1427	1.3465
Raw jojoba oil + mineral oil base stock (50:50) + aromatic amine-B (0.5%)	0.0140	0.0420	0.1234	0.3702	0.1720	0.1600	0.2161	0.2923
Raw jojoba oil + mineral oil base stock (50:50) + aromatic amine-C (0.5%)	0.0313	0.1982	0.2109	0.3164	0.1120	0.0920	0.1897	0.2571

at 100°C cover the requirements. Jojoba oil is a low viscosity oil of 6 cSt at 100°C and therefore, its utility as a base stock is limited. Jojoba oil's wax ester structure, with a *cis* stereo chemistry, makes it reactive in a variety of chemical transformations, including sulfur chlorination, sulfurization, hydrogenation, isomerization and epoxidation. Jojoba oil when sulfurized is good for lubrication in automotive transmissions.

The utilization of jojoba oil in lubricating oil formulations can be widened if these chemical modifications can provide products of different viscosity levels. With this in view, partial sulfurization of jojoba oil was carried out to levels of 0.2-2.0% sulfur. The sulfur content of samples A1-A6 varied from 0.198 to 1.74%

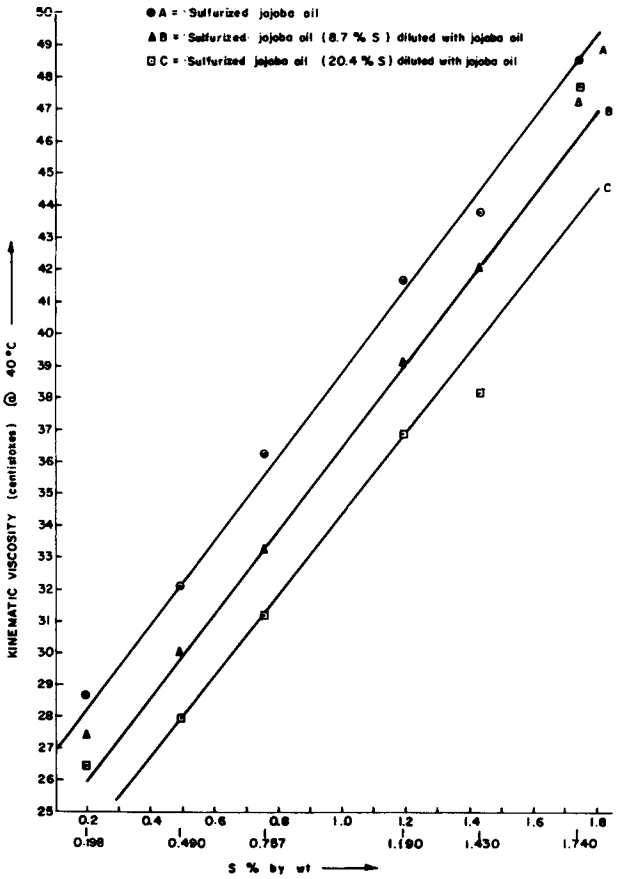

FIG. 2. Effect of partial sulfurization of jojoba oil on viscosity.

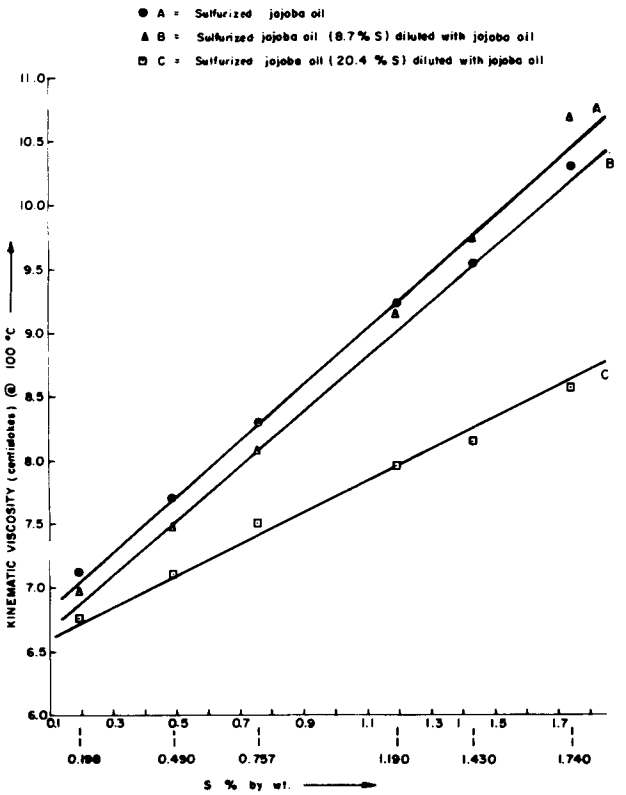

FIG. 3. Effect of partial sulfurization of jojoba oil on viscosity.

and the corresponding viscosities at 100°C were 7.12 to 10.28 cSt. The viscosity values at different sulfur levels at 40°C and 100°C are plotted in Figures 2 and 3, respectively. Blends of sulfurized jojoba oil SJO-10 (10% S treatment level) or SJO-26 (26% S treatment level) with jojoba oil as a base stock, to get the same sulfur levels as in samples A1 to A6, were also prepared and viscosities of these blends were determined. The values at 40°C and 100°C are also plotted in Figures 2 and 3.

At the same sulfur levels, the samples prepared with the direct addition of the required amount of sulfur generally were found to have higher viscosities than the blends with SJO-10 and SJO-26. In our earlier studies, it was found that even though the sulfur level was the same, the corrosion tendency increased with sulfur treatment level. At 1% sulfur level in a blend, SJO-10 gave a copper strip corrosion value of 1b whereas SJO-26 gave a 4C corrosion value. Even at 1.74% sulfur level, the blend containing SJO-10 gave a copper strip corrosion value of 1b only. The corrosion tendency can thus be attributed to the difference in composition of SJO with respect to the reactive sulfur components. Therefore, the A-6 sample of 2% sulfur treatment level containing 1.74% sulfur is not expected to show any corrosion tendency. Partial sulfurization seems to be a good approach to improve the viscosity of jojoba oil.

This study suggests that the limitations of jojoba oil can be overcome and modified jojoba oil can be used as a blending component in lubricating oil formulations for the purpose of conserving mineral oil base stocks. In applications where pour point is not a critical requirement, jojoba oil has a potential to replace mineral oil.

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REFERENCES

1. Ramesh, J., and J.N. Maggo, in *Towards a Perspective on Energy Demand and Supply in India in 2004/05,* Advisory Board of Energy, Government of India, (1985), pp. 222-224.
2. Roorda, J., in *Proc. 10th World Petroleum Congress,* (1979), pp. 339-342.
3. Singh, H., P.C. Gupta, M. Anwar, G.S. Chowdhry, K. Kishore, R.S. Kaushik, M.M. Kumar and Mohan Lal, *Petr. Asia* 7:150 (1984).
4. *Jojoba, New Crop for Arid Lands, New Raw Material for Industry,* National Academic Press, Washington, (1985), pp. 13-36.

5. Gruse, W.A., and D.R. Steven, in *Chemical Technology of Petroleum*, 3rd ed., McGraw Hill Book Co., London, (1960), pp. 310–316.
6. Chaudhry, A., in *Study of* Simmondsia chinensis *(Jojoba) Oil and Its Derivatives*, Ph.D. Thesis, Garhwal University, (1985), pp. 187–197.
7. Bhatia, V.K., A. Chaudhry, A. Masohan, R.P.S. Bisht and G.A. Sivasankaran, *J. Am. Oil Chem. Soc. 65*:1502 (1988).
8. Estefan, R.M., in *Jojoba Oil as a Possible Lubricant*, 74th Annual Meeting of AOCS, Chicago, (1983).
9. Abon el Naga, H.H., and A.E.M. Salem, *Lubn. Engg. 42*:210 (1986).
10. Miwa, T.K., and J.A. Rothfus, *Proc. 3rd Int. Conf. Jojoba* (1978), pp. 243–267.
11. Miwa, T.K., J.A. Rothfus and E. Dimitroff, *J. Am. Oil. Chem. Soc. 56*:765 (1979).
12. Yaron, A., *Scie, Activities 1976, Jojoba Happenings 23*:29 (1978).
13. Kampf, A., S. Grinberg and A. Galun, *J. Am. Oil Chem. Soc. 63*:246 (1986).
14. Kuno, Y., K. Tomito, K. Katsura and S. Ohta, *Proc. 4th Int. Conf. Jojoba*, (1980), pp. 239–265.

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